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(54) Title: METHODS AND COMPOSITIONS RELATING TO HALOGENATED POLYCARBONATE HAVING IM- PROVED THERMAL STABILITY (57) Abstract The thermal stability of a halogenated polycarbonate, or an article molded therefrom, is improved by incorporating a trisaryl phosphite into the halogenated polycarbonate in an amount of 200 to 1,500 weight parts per million. The thermal stabilizing effect of the phosphite is apparent in a reduced level of yellowness in the halogenated polycarbonate or molded article. Amounts of trisaryl phosphite less than 200 ppm or greater than 1,500 ppm do not give the desired stabilizing effect. Trisaryl phosphite which has performed its stabilizing effect is present as trisaryl phosphate.		

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METHODS AND COMPOSITIONS RELATING TO HALOGENATED
POLYCARBONATE HAVING IMPROVED THERMAL STABILITY

5 This invention pertains to methods of
stabilizing halogenated polycarbonate against the
effects of thermal degradation and aging, to halogenated
polycarbonate compositions having a desirably high level
of thermal stability, and to objects molded from such
10 compositions.

Polycarbonate has found many uses because it
combines, in general, a high level of heat resistance,
impact resistance and dimensional stability with good
15 insulating and non-corrosive properties, and it is
easily molded. Halogenated polycarbonate is
particularly known for its heat resistance and for its
high glass transition temperature (T_g), which typically
exceeds 175°C. T_g is the temperature or temperature
20 range at which an amorphous polymeric material shows an
abrupt change in physical properties, including, for
example, mechanical strength. T_g can be determined, for
example, by differential scanning calorimetry. The T_g
25 associated with halogenated polycarbonate is higher than

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that of most other thermoplastics and makes halogenated polycarbonate a logical choice for use in molding articles which must withstand high service temperatures. However, when halogenated polycarbonate is used in a high service-temperature environment, it often shows a reduction in the level of its other desirable properties because of the thermal aging and degradation it experiences in such environment.

Various stabilizers and stabilizer packages have been proposed in the past for the purpose of attempting to ameliorate the degradative effects suffered by halogenated polycarbonate or co-polycarbonate when it is exposed to high temperatures during processing. For example, Cleveland, U.S. Patent Number 3,733,296 discloses as a stabilizer for halogenated polycarbonate the use of phosphite together with barium, strontium and/or calcium carbonate, and Factor, U.S. Patent Number 3,763,063 discloses as a stabilizer for halogenated polycarbonate the use of phosphite in a mixture with an alkanolic acid and a salt of an alkanolic acid. And, although Fritz, U.S. Patent Number 3,305,520 and Rasberger, U.S. Patent Number 4,321,218 both disclose the use of a phosphite as a stabilizer for polycarbonate, neither recognizes any special conditions under which such a phosphite should be employed when it is used in a halogenated polycarbonate. Further, the employment of a stabilizer which is effective to protect polycarbonate from high temperature during processing and/or fabrication may not be equally applicable to the achievement of thermal stability during a lengthy exposure of polycarbonate to the degradative effects of a high service temperature.

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Accordingly, it would be desirable to have compositions, and methods for making those compositions, wherein a phosphite could be employed alone as a stabilizer in a halogenated polycarbonate for the purpose of imparting resistance to the undesirable, degradative effects resulting from extended exposure of such composition to high temperature.

In one aspect, this invention involves a composition of matter containing halogenated polycarbonate and 200 to 1,500 parts per million, by weight of the total composition, trisaryl phosphite. In a further aspect, this invention involves a film, sheet, molded or thermoformed article, or other object which has been thermally aged, comprising, in admixture, (a) brominated polycarbonate and (b) 200 parts per million to 1,500 parts per million, by weight of the total composition, (i) trisaryl phosphite, (ii) trisaryl phosphate, or (iii) a mixture thereof. This invention also involves a composition of matter comprising a polycarbonate which contains 10-30 percent bromine by weight and has been stabilized against the effects of thermal degradation, said composition being characterized in that an article molded therefrom has a Yellowness Index of no more than 13, as measured according to ASTM Designation D 1925-70, after 1,512 hours of thermal aging in a forced air oven at 130°C. Yet another aspect of this invention is a method of stabilizing a brominated polycarbonate against the effects of thermal degradation comprising forming a composition by admixing with said brominated polycarbonate 200 parts per million to 1,500 parts per million trisaryl phosphite.

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5 It has been found, for example, that an article molded from a composition containing a halogenated polycarbonate (such as a brominated segmented block copolycarbonate) and a stabilizing amount of trisaryl phosphite displays a much lower level of degradative effects from thermal aging than a halogenated polycarbonate composition which contains an insufficient or too great an amount of trisaryl phosphite. 10 Stabilization against the occurrence of such degradative effects of thermal aging can be demonstrated, for example, by a lower Yellowness Index (as measured by ASTM Designation D 1925-70) in an article molded from a halogenated polycarbonate protected by 200 to 1,500 ppm 15 trisaryl phosphite, by weight of the total composition, as opposed to a halogenated polycarbonate containing other amounts of trisaryl phosphite or other amounts of other stabilizing additives.

20 The methods of this invention are useful for producing the compositions of this invention, such compositions being useful, for example, in the production of films, fibers, extruded sheets, multi-layer laminates, oxygen-nitrogen separation membrane, 25 and molded or shaped articles of virtually all varieties, particularly apparatus which are transparent (i.e. having more than 80 percent light transmittance when measured according to ASTM Designation D 1746-70), 30 and particularly parts for the transportation and appliance industries such as motor vehicle headlamp lenses, aircraft canopies, and autoclavable medical apparatus.

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Figure 1 is a plot of yellowness index vs. time of exposure in hours to 130°C heat for unhalogenated polycarbonate containing various levels of trisaryl phosphite.

5 Figure 2 is a plot of yellowness index vs. time of exposure in hours to 130°C heat for halogenated polycarbonate containing various levels of trisaryl phosphite.

10 Figure 3 is a plot of yellowness index after 1,512 hours of exposure to 130°C heat vs. level of trisaryl phosphite for both halogenated and unhalogenated polycarbonate containing various levels of trisaryl phosphite.

15 Figure 4 is a plot of weight average molecular weight vs. time of exposure in hours to 130°C heat for unhalogenated polycarbonate containing various levels of trisaryl phosphite.

20 Figure 5 is a plot of weight average molecular weight vs. time of exposure in hours to 130°C heat for halogenated polycarbonate containing various levels of trisaryl phosphite.

25 Figure 6 is a plot of weight average molecular weight after 1,512 hours of exposure to 130°C heat vs. level of trisaryl phosphite for unhalogenated polycarbonate containing various levels of trisaryl phosphite.

30 Figure 7 is a plot of weight average molecular weight after 1,512 hours of exposure to 130°C heat vs. level of trisaryl phosphite for halogenated polycarbonate containing various levels of trisaryl phosphite.

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The compositions of this invention contain halogenated polycarbonate admixed with trisaryl phosphite in an amount of 200 to 1,500 parts per million ("ppm"), by weight of the total composition. In a
5 preferred formulation, the compositions of this invention contain trisaryl phosphite in an amount of 200 to 800 ppm, by weight of the total composition, admixed with halogenated polycarbonate. The compositions of
10 this invention have a weight average molecular weight, determined for example by gel permeation chromatography ("GPC"), of 10,000 to 100,000, advantageously 25,000 to 40,000, and preferably 26,000 to 32,000.

15 Preparation of the compositions of this invention can be accomplished by any suitable mixing means known in the art. Typically, trisaryl phosphite is dry blended in particulate form with sufficient
20 agitation to obtain thorough distribution thereof within the halogenated polycarbonate. Compounding by means of mixing rolls, a dough-mixer or a Banbury mixer can be useful in this context, or, if desired, the dry-blended formulation can further, but need not, be melt mixed in
25 an extruder. When melt mixed, the compositions of this invention are preferably prepared at as low a temperature as possible over the T_g of the halogenated polycarbonate at which the components are processible, for example in the range of 575-620°F (302-327°C).
30 Trisaryl phosphite and halogenated polycarbonate can also be admixed in solution, and methylene chloride, acetone, benzaldehyde or heptane are useful solvents for such purpose. The compositions can then be separated from the solvent by known methods such as devolatilization or use of an anti-solvent.

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Alternatively, a master batch formulation can be prepared containing halogenated polycarbonate with which trisaryl phosphite is admixed wherein halogenated polycarbonate is present in only a minor proportion, e.g. 20 percent. Although the master batch formulation may contain more than 1,500 ppm trisaryl phosphite, it is more readily available for storage or shipment in commerce, and the master batch can, at the time of use, be diluted with additional halogenated polycarbonate to obtain the relative content levels specified above.

The compositions of this invention can be formed into articles or molded using conventional techniques such as compression, injection, calendering, vacuum forming, extrusion and/or blow molding techniques, alone or in combination. The compositions can also be formed into films, fibers, multi-layer laminates or extruded sheets on any machine suitable for such purpose.

The methods of this invention are those in which a composition is formed by admixing with halogenated polycarbonate trisaryl phosphite in an amount of 200 to 1,500 ppm, and preferably in an amount of 200 to 800 ppm, by weight of the total composition. Use of trisaryl phosphite in such amounts substantially prevents the occurrence, to an undesirable extent, of the effects resulting from thermal degradation and aging to which such composition may be subjected. For example, the methods of this invention control to a desirable level formation or increase of color bodies in a halogenated polycarbonate composition containing a stabilizing amount of triaryl phosphite as compared to

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compositions not so stabilized. The color stability which is imparted by the methods, and to the compositions, of this invention can be demonstrated, for example, by comparing the level of Yellowness Index ("Y.I.", as measured by ASTM Designation D 1925-70) found in the compositions made by the methods of this invention (being the compositions of this invention) with that found in compositions outside of this invention.

The presence of trisaryl phosphite in a composition in an amount less than 200 ppm or exceeding 1,500 ppm typically does not control to desirable levels in halogenated polycarbonate the effects of thermal degradation, for example those relating to color stability. Use of trisaryl phosphite in amounts greater than 1,500 ppm may also contribute, in a composition, to degradation from heat exposure in the form of molecular weight loss. The molecular weight degradation which can result from admixing with halogenated polycarbonate more than 1,500 ppm trisaryl phosphite, by weight of the total composition, can be demonstrated by comparing molecular weights of modified and unmodified polycarbonates using GPC.

The stability which trisaryl phosphite imparts to halogenated polycarbonate is protection against a reduced level of desirable properties, or an increased level of undesirable properties, such as may result from thermal aging of an article molded therefrom. An example of thermal aging is a process wherein heat promotes the reaction of oxygen with the polymer to form hydroperoxides with the consequent breakdown of the polymeric backbone resulting in chain scission and/or

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the development or increase, for example, of colored bodies. Thermal aging can occur in any environment, or by any mechanism, where halogenated polycarbonate is exposed to heat in sufficient quantity to promote such oxidative reaction and/or other forms of degradation
5 such as discoloration and/or molecular weight loss. Thermal aging is typically said to have occurred when a composition of this invention, or a molded article or other object comprising such composition, is exposed to heat of at least 125°C for a period of at least 250
10 hours.

When a film, sheet, article, fiber or other object formed or molded from a composition of this
15 invention is exposed to thermal aging, and the trisaryl phosphite present therein performs its intended function of reducing or preventing the degradative effects of the thermal aging, the trisaryl phosphite is converted to the corresponding trisaryl phosphate. Consequently,
20 when a film, sheet, article, fiber or other object formed from a composition of this invention is analyzed after having been exposed to thermal aging, it can be analyzed to determine the content of trisaryl phosphite, trisaryl phosphate or both. The longer and more harsh
25 the thermal aging is that the film, sheet, article, fiber or other object has been exposed to, the greater will be the quantity of trisaryl phosphite which has been converted to trisaryl phosphate. In a film, sheet,
30 article, fiber or other object formed from the compositions of this invention, the content of (a) trisaryl phosphite, (b) trisaryl phosphate, or (c) a mixture of the two should therefore be between 200 to 1,500 ppm, and preferably between 200 to 800 ppm, by weight of the total composition. After thermal aging, a

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film, sheet, article fiber or other object formed from the compositions of this invention should have a Yellowness Index of less than 15, and preferably less than 12, as measured according to ASTM Designation D 1925-70; and should also have a decrease, if any, in
5 weight average molecular weight, as determined for example by GPC, of less than 5 percent, advantageously less than 4 percent, preferably less than 3 percent, and more preferably no molecular weight loss at all.

10 The compositions of this invention, and the compositions made by the methods of this invention, are substantially free of additives, other than trisaryl phosphite, which inhibit the effects of thermal aging.
15 Other such additives include, for example, benzoates, carbonates, or alkanolic acids or salts thereof. The presence of such other additives may, for example, cause lower impact strength or reduce light transmittance in an article molded from a halogenated polycarbonate
20 composition containing them. It is found that when trisaryl phosphite, as opposed to other organophosphorous compounds, is used alone in a stabilizing amount as the stabilizing additive in
25 halogenated polycarbonate, good stability, for example a reduced level of color formation or increase, is obtained without a need for incorporating additional additives, such as the salts, acids or benzoates mentioned above.

30

Halogenated Polycarbonate. Halogenated polycarbonate is produced by any of the conventional processes known in the art for the manufacture of aromatic polycarbonates. Generally, aromatic polycarbonates are prepared by reacting an aryl diol or

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dihydric phenol with a carbonate precursor, such as phosgene, a haloformate or a carbonate ester.

5 A preferred method for preparing aromatic polycarbonates involves the use of a carbonyl halide, such as phosgene, as the carbonate precursor. This method involves passing phosgene gas into a reaction mixture containing an activated dihydric phenol, or a nonactivated dihydric phenol and an acid acceptor, for
10 example pyridine, dimethyl aniline, quinoline. The acid acceptor may be used undiluted or diluted with inert organic solvents, such as methylene chloride, chlorobenzene or 1,2-dichloroethane. Tertiary amines are advantageous since they are good solvents as well as
15 acid acceptors during the reaction.

The temperature at which the carbonyl halide reaction proceeds may vary from below 0°C to 100°C. The reaction proceeds satisfactorily at temperatures from
20 room temperature to 50°C. Since the reaction is exothermic, the rate of phosgene addition may be used to control the temperature of the reaction. The amount of phosgene required will generally depend upon the amount
25 of dihydric phenol present. Typically, one mole of phosgene will react with one mole of dihydric phenol to form the polycarbonate and two moles of HCl. The HCl is in turn taken up by the acid acceptor.

30 Another method for preparing aromatic polycarbonates involves adding phosgene to an alkaline aqueous suspension of dihydric phenols. This is done in the presence of inert solvents such as methylene chloride, 1,2-dichloroethane. Quaternary ammonium compounds may be employed to catalyze the reaction.

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Yet another method for preparing such aromatic polycarbonates involves the phosgenation of an agitated suspension of an anhydrous alkali salt of an aryl diol in a nonaqueous medium such as benzene, chlorobenzene or toluene. The reaction is illustrated by the addition of phosgene to a slurry of the sodium salt of, for example, 2,2-bis(4-hydroxyphenyl)propane ("Bisphenol A" or "Bis A") in an inert polymer solvent such as chlorobenzene.

In general, a haloformate such as the bishaloformate of Bisphenol A may be used in place of phosgene as the carbonate precursor in any of the methods described above.

When a carbonate ester is used as the carbonate precursor in the polycarbonate-forming reaction, the materials are reacted at temperatures in excess of 100°C, for times varying from 1 to 15 hours. Under such conditions, ester interchange occurs between the carbonate ester and the dihydric phenol used. The ester interchange is advantageously consummated at reduced pressures on the order of from 10 to 100 millimeters of mercury, preferably in an inert atmosphere such as nitrogen or argon.

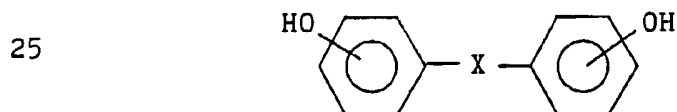
Although the polymer-forming reaction may be conducted in the absence of a catalyst, one may, if desired, employ a typical ester exchange catalyst, such as metallic lithium, potassium, calcium or magnesium. The amount of such catalyst, if used, is usually small, ranging from 0.001 percent to 0.1 percent, based on the weight of the dihydric phenols employed.

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In the solution methods of preparation, the aromatic polycarbonate emerges from the reaction in either a true or pseudo solution depending on whether an aqueous base or pyridine is used as an acid acceptor. The product may be precipitated from the solution by
5 adding a nonsolvent, such as heptane or isopropanol, or the solution may be heated, typically under reduced pressure, to evaporate the solvent.

10 The methods and reactants described above for preparing aromatic polycarbonates, and aromatic polycarbonates for use as the halogenated polycarbonate of this invention, are discussed in greater detail in Schnell, U.S. Patent Number
15 3,028,365; Campbell, U.S. Patent Number 4,384,108; Glass, U.S. Patent Number 4,529,791; and Grigo, U.S. Patent Number 4,677,162.

20 Aromatic polycarbonates can be prepared from aryl diols such as those represented, for example, by the formula:



wherein X is a divalent C_1 - C_{15} hydrocarbon radical, a
30 single bond, -O-, -S-, - S_2 -, -SO-, - SO_2 -, or -CO-. Each aromatic ring may additionally contain, instead of hydrogen, up to four substituents such as C_1 - C_{20} alkyl, aryl, alkaryl or aralkyl hydrocarbon radicals, or C_1 - C_{20} alkoxy or aryloxy radicals, or halo radicals. More than one of the above described aryl diols, or two or more

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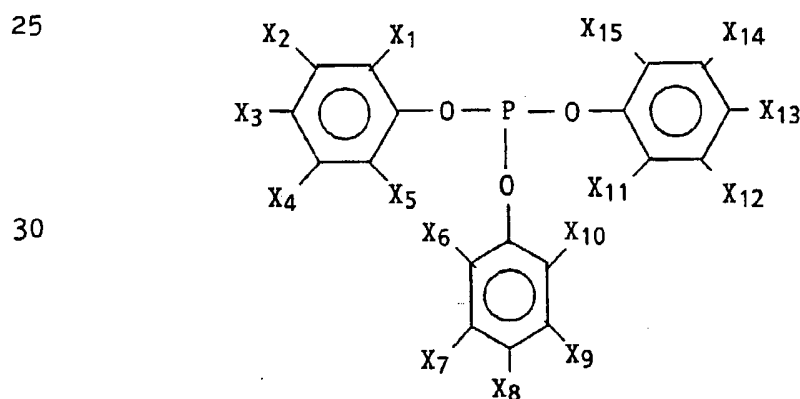
other dihydroxy compounds, can be used if it is desired to prepare aromatic co-polycarbonates. Aromatic co-polycarbonates can also be produced, for example, when a bisphenol is reacted with a carbonic acid derivative and a polydiorganosiloxane containing α,ω -bishydroxyaryloxy terminal groups to yield a siloxane/carbonate block copolymer (as are discussed in greater detail in Paul, U.S. Patent Number 4,569,970, or when a bisphenol is reacted with a bis(ar-haloformylaryl) carbonate to yield an alternating co-polyestercarbonate. The bis(ar-haloformylaryl) carbonate is formed by reacting a hydroxycarboxylic acid with a carbonic acid derivative under carbonate forming conditions, such co-polyestercarbonates being discussed in greater detail in Swart, U.S. Patent Number 4,105,533.

The halogenated polycarbonate for use in this invention can be an aromatic polycarbonate, an aromatic co-polycarbonate, or blend of one or more of each. It is preferred that such aromatic polycarbonate, aromatic co-polycarbonate or blend contains therein from 10 percent to 30 percent, by weight, of halogen, such as chlorine, bromine or iodine, bound to a polymer chain. It is preferred that the halogen is bound to an aromatic ring. The preferred halogenated polycarbonate for purposes of this invention is brominated polycarbonate.

A preferred brominated polycarbonate for use in this invention is that which is prepared by the processes disclosed in Marks, U.S. Patent Number 4,902,758, wherein high molecular weight segmented block co-polycarbonates are prepared from diphenols, such as Bisphenol-A, and tetrahalogenated diphenols, such as 2,2-bis(3,5-dibromo, 4-hydroxyphenyl)propane

("Tetrabromo Bisphenol-A" or "TBBA"). Segmented block co-polycarbonates from diphenols and tetrahalogenated diphenols can be prepared by phosgenation, under interfacial reaction conditions, initially at a higher pH such as 12 to 13, during which diphenol oligomers are formed, and thereafter at a lower pH such as 10 to 11, during which tetrahalogenated diphenol bischloroformates are formed, followed by copolymerization utilizing an activated pyridine catalyst such as 4-dimethylaminopyridine. Alternatively, diphenol polycarbonate oligomers and tetrahalogenated diphenol chloroformates may be coupled, utilizing an activated pyridine catalyst such as 4-dimethylaminopyridine, to prepare segmented block co-polycarbonates. Preferred formulations of such segmented block co-polycarbonates are those prepared from Bisphenol-A and TBBA wherein the molar ratio of Bisphenol-A to TBBA is from 2:1 to 4:1.

20 Trisaryl Phosphite. The trisaryl phosphites useful in this invention contain a substituted or unsubstituted phenyl ring bonded to each of the three oxygen atoms bonded to phosphorous, and can be represented by a structure such as

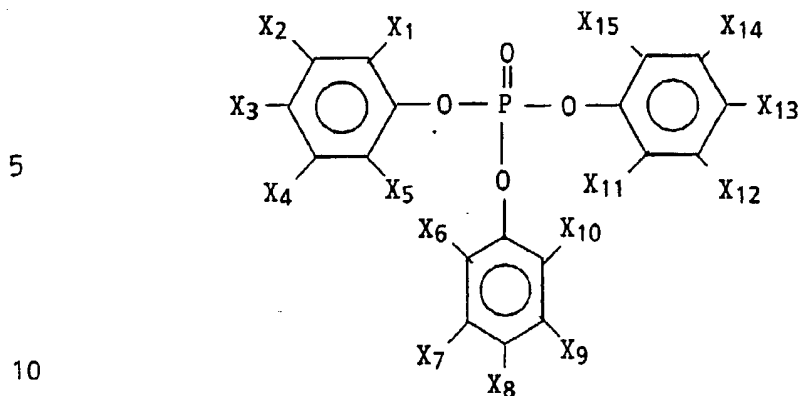


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where X_1 to X_{15} is each independently hydrogen or an alkyl, aryl, alkaryl or aralkyl radical of one to ten carbon atoms. X can, for example, be an ethyl, propyl, butyl, amyl, hexyl, octyl, nonyl or decyl radical; can be a cycloalkyl radical such cyclohexyl, 2- or 4-methylcyclohexyl or cyclopentyl; or can be a phenyl, naphthyl, tolyl or xylyl radical. A mixture of more than one of such trisaryl phosphites can be used herein as well. A trisaryl phosphite can be made by reacting three or more moles of the desired substituted or unsubstituted phenol(s) with a mole of a phosphorous trihalide, such as PCl_3 , and three moles of a halide acceptor, preferably an organic base such as pyridine or dimethylaniline. Ammonia or triethylamine may also be useful as the base in such reaction. The trihalide, in a solvent such as diethyl ether, pentane or benzene, is added dropwise to a well stirred solution of the phenol(s) and the base which is cooled to $10^\circ C$. The organic ammonium halide is filtered off, and the tertiary ester of phosphorous acid is purified by vacuum distillation. A preferred trisaryl phosphite is tris (2,4-di-t-butylphenyl) phosphite, which is available as Irgafos™ 168 phosphite or as P168™ phosphite from Ciba-Geigy Corp.

The trisaryl phosphite described above is converted to the corresponding trisaryl phosphate by the degradative effects of thermal aging on a halogenated polycarbonate with which the phosphite is admixed. The trisaryl phosphate can be represented by a structure such as

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where X is as set forth above.

15 The compositions of this invention are substantially free of any color stabilizing additives other than trisaryl phosphite, but they can further contain conventional thermoplastic polymer additives such as fillers, dyes, flame retarding agents,

20 reinforcing agents, softeners, mold-release agents, seed-forming agents, pigments, plasticizers, antistatic agents, UV absorbers, lubricants, in conventional amounts generally not exceeding 25 percent by weight of the total composition.

25

Illustrative Embodiments. To illustrate the practice of this invention, examples of preferred embodiments thereof are set forth below. It is not intended, however, that these examples (Examples 1-4)

30 should in any manner limit the scope of this invention. Some of the particularly desirable features of this invention may be seen by contrasting the characteristics of Examples 1-4 with those of various controlled formulations (Controls A-H) which do not possess the

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features of, and are not therefore embodiments of, this invention.

5 Controls A-H and Examples 1-4 were prepared by admixing various amounts of tris (2,4-di-t-butylphenyl) phosphite with a polycarbonate. In Controls A-F, Bisphenol-A homopolycarbonate was used. In Controls G-H and Examples 1-4, brominated segmented block co-polycarbonate made from Bisphenol-A and TBBA by the processes disclosed in U.S. Patent Number 4,902,758 was used. Controls G-H and Examples 1-4 each has a T_g of at least 175°C and each contains 25 percent bromine by weight. The amount of tris (2,4-di-t-butylphenyl) phosphite contained in Controls A-H and Examples 1-4 is shown in Tables I-IV below in ppm by total weight of those compositions, respectively.

20 Flakes of the Bisphenol-A polycarbonate, in the case of Controls B-F, and flakes of the brominated segmented block co-polycarbonate in the case of Control H and Examples 1-4, were tumble blended with epoxidized soybean oil as a tackifier for the trisaryl phosphite additive. Flakes of the Bisphenol-A polycarbonate, in the case of Controls A-F, and flakes of the brominated segmented block co-polycarbonate in the case of Controls G-H and Examples 1-4, were then tumble blended with tris (2,4-di-t-butylphenyl) phosphite, and the formulation was then processed on a 1½" single-screw Killian extruder at 575-620°F (302-327°C) to intimately mix the materials. After extrusion, each formulation was injection molded on an Arburg 70 under the following conditions: screw speed: 300 rpm; feed temperature: 300°C; barrel temperature: 300°C; nozzle temperature: 300°C; injection pressure: 45 bar; back pressure: 45

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bar; holding pressure: 45 bar; and mold temperature: 175-200°F (79-93°C). The mold was stainless steel and produces discs of 6.2 cm diameter and 0.3 cm thickness.

5 The discs were placed in a forced-air oven for continuous thermal aging at 130°C, and all measurements were repeated after varying lengths of time with the results as also shown in Tables I-IV.

10 The Yellowness Index of a disc molded from each formulation was measured according to ASTM Designation D 1925-70 using a Hunter Lab Colorimeter Model D25-9. The weight average molecular weight of each disc was measured using GPC. Trisaryl phosphite and trisaryl
15 phosphate content was measured for Controls G-H and Examples 1-4 using reverse phase liquid chromatography.

20

25

30

Table I
 Trisaryl Phosphite Content and Yellowness Index
 of Bisphenol-A Polycarbonate Samples (Controls A-F)

	Tris (2,4-di- t-butyl phenyl) phosphite, ppm	Yellowness Index at								
		0 hours	168 hours	336 hours	504 hours	672 hours	840 hours	1,152 hours	1,320 hours	1,512 hours
Control A	0	4.9	6.2	6.4	6.7	6.7	7.1	7.4	7.6	7.9
Control B	200	4.3	5.3	5.4	5.7	5.9	7.3	6.4	6.6	7.0
Control C	400	3.9	4.9	5.1	5.5	5.7	5.9	6.2	6.4	6.7
Control D	800	3.6	4.5	4.6	5.1	5.4	5.6	6.0	6.1	6.5
Control E	1,500	3.2	4.1	4.2	4.8	5.0	5.4	5.9	6.2	6.8
Control F	2,000	3.1	3.9	4.2	4.7	5.0	5.5	6.0	6.2	6.9

Table II
 Trisaryl Phosphite Content and Yellowness Index
 of Brominated Polycarbonate Samples
 (Controls G-H and Examples 1-4)

	Tris (2,4-di- t-butyl) phenyl) phosphite, ppm	Yellowness Index at								
		0 hours	168 hours	336 hours	504 hours	672 hours	840 hours	1,152 hours	1,320 hours	1,512 hours
Control G	0	6.8	9.1	10.3	11.1	12.2	12.5	13.4	13.8	14.6
Example 1	200	5.1	6.4	7.1	7.7	8.1	8.2	8.7	8.9	9.4
Example 2	400	4.9	6.0	6.7	7.5	7.9	8.0	8.4	8.6	9.1
Example 3	800	5.8	7.3	8.0	8.8	9.5	9.8	10.5	10.7	11.6
Example 4	1,500	5.2	6.4	7.1	8.3	9.0	9.5	10.5	11.2	12.2
Control H	2,000	5.9	16.4	21.3	25.0	27.4	29.4	32.0	34.2	37.0

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Table III
 Trisaryl Phosphite Content and Molecular Weight
 of Bisphenol-A Polycarbonate Samples (Controls A-F)

	'Tris (2,4-di- t-butyl phenyl) phosphite, ppm	Molecular Weight at								
		0 hours	168 hours	336 hours	504 hours	672 hours	840 hours	1,152 hours	1,320 hours	1,512 hours
Control A	0	34,615	35,056	35,970	36,084	35,628	35,567	35,429	34,800	36,306
Control B	200	34,983	35,478	35,834	35,385	35,326	36,133	34,304	35,729	36,379
Control C	400	35,180	35,514	35,910	35,975	35,888	36,310	35,420	35,051	36,330
Control D	800	34,944	35,224	35,947	35,874	35,521	36,490	33,964	34,671	35,917
Control E	1,500	34,865	35,513	35,865	35,823	35,128	35,871	33,806	35,078	35,723
Control F	2,000	34,154	35,311	35,735	35,578	35,087	35,195	34,972	35,528	35,184

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Table IV
 Trisaryl Phosphite Content and Molecular Weight
 of Brominated Polycarbonate Samples
 (Controls G-H and Examples 1-4)

	Tris (2,4-di- t-butyl phenyl) phosphite, ppm	Molecular Weight at								
		0 hours	168 hours	336 hours	504 hours	672 hours	840 hours	1,152 hours	1,320 hours	1,512 hours
Control G	0	27,818	28,058	28,706	29,251	28,951	28,568	28,062	27,639	28,754
Example 1	200	29,498	29,506	29,970	29,861	29,602	29,620	28,420	29,630	30,353
Example 2	400	29,464	29,453	29,743	29,793	29,604	29,515	29,411	29,762	30,098
Example 3	800	29,251	29,071	29,385	29,173	28,994	29,285	28,979	28,858	29,903
Example 4	1,500	29,453	29,333	29,566	29,622	29,080	28,651	28,506	28,023	28,561
Control H	2,000	28,740	27,107	25,564	25,907	24,173	24,530	23,500	28,561	22,547

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The results of the Yellowness Index and molecular weight tests show that when a trisaryl phosphite [such as tris (2,4-di-t-butylphenyl) phosphite] is admixed in an amount of 200 ppm to 1,500 ppm, by weight of the total composition formed therefrom, with halogenated polycarbonate (such as brominated segmented block co-polycarbonate), the color of an article molded from such composition is stabilized against the degradative effects of thermal aging. However, these results also show that when a trisaryl phosphite is used in an amount less than 200 ppm or exceeding 1,500 ppm to stabilize a brominated polycarbonate, the discoloration effects of thermal degradation are not reduced to the desired levels, and the presence of the trisaryl phosphite in an amount greater than 1,500 ppm causes a loss in weight average molecular weight.

As a basis for comparison, the data reported above show that when a trisaryl phosphite is used in an amount in the zero to 2,000 ppm range to stabilize a non-brominated polycarbonate, such as a Bisphenol-A polycarbonate, the level of degradation, as shown by Yellowness Index or molecular weight, varies with the level of stabilizer over an insignificant range. For example, the discs molded from Controls A-F (Bisphenol-A polycarbonate) has Yellowness Index readings after 1,512 hours of aging varying only from 7.9 (0 ppm trisaryl phosphite) to 6.9 (2,000 ppm trisaryl phosphite). Similarly, Control F, which contain 2,000 ppm of trisaryl phosphite, show no decrease in molecular weight after 1,512 hours of aging. The limited range of the effect of a trisaryl phosphite on Bisphenol-A

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polycarbonate is also shown in the tight cluster of plot lines in Figures 1 and 4.

5 The slight variation in the extent of control
of Yellowness Index, and the absence of molecular weight
loss at the 2,000 ppm level, resulting from the use of a
trisaryl phosphite to stabilize Bisphenol-A
polycarbonate, does not suggest the criticality of the
amount of trisaryl phosphite needed to properly
10 stabilize halogenated polycarbonate. Note in Figure 2
the sharp break, at 0 ppm and at 2,000 ppm, in the line
representing for the brominated polycarbonate the
Yellowness Index readings at 1,512 hours of aging. The
line representing the Yellowness Index readings for
15 Bisphenol-A polycarbonate in Figure 3, however, is
nearly flat. Correspondingly, the sharp drop in
molecular weight for the brominated polycarbonate, when
trisaryl phosphite is used at the 2,000 level, as shown
in Figure 7, can be compared with the nearly flat line
20 for the molecular weight of Bisphenol-A polycarbonate
shown in Figure 6.

 When the polycarbonate to be stabilized by
25 trisaryl phosphite is halogenated the amount of triaryl
phosphite used does make a significant difference. For
example, the discs molded from Controls G-H (brominated
polycarbonate) showed a Yellowness Index, and Control H
showed a molecular weight, which is notably less
30 desirable than the respective readings for the discs
molded from Examples 1-4. Control G (0 ppm trisaryl
phosphite) and Control H (2,000 ppm trisaryl phosphite)
fell outside the critical range of 200-1,500 ppm
trisaryl phosphite for brominated polycarbonates and
therefore have undesirably high Yellowness Index

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readings at 1,512 hours of 14.6 and 37.0, respectively. Examples 1-4, on the contrary, had Yellowness Index readings at 1,512 hours which varied only from 9.4 (200 ppm) to 12.2 (1,500 ppm). The Yellowness Index reading for Control H was 3 times that for Example 4 at 1,512
5 hours. This variance in Yellowness Index readings according to amount of trisaryl phosphite used can be observed in Figure 2. Note in Figure 2 the tight cluster of the plot lines for Examples 1-4 (200-1,500
10 ppm trisaryl phosphite, respectively) as compared to the divergence of the plot lines representing 0 and 2,000 ppm trisaryl phosphite, respectively. The molecular weight readings for Control H and Examples 1-4 showed similar results, as can be seen from Figure 5.

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It is apparent from this data that when trisaryl phosphite is used to stabilize halogenated polycarbonate against degradation from thermal aging, it is critical to use it in an amount ranging from 200 to
20 1,500 ppm, based on the total weight of the composition. The prior art dealing with use of a phosphite as a stabilizer for polycarbonate does not recognize the criticality of these limits, and use of a trisaryl
25 phosphite as a stabilizer for halogenated polycarbonate over the entire ranges taught by the prior art will not achieve the reduced levels of the effects of thermal degradation attained herein.

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It is within the skill in the art to practice this invention in numerous modifications and variations in light of the above teachings. It is, therefore, to be understood that the various embodiments of this invention described herein may be altered without

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departing from the spirit and scope of this invention as defined by the appended claims.

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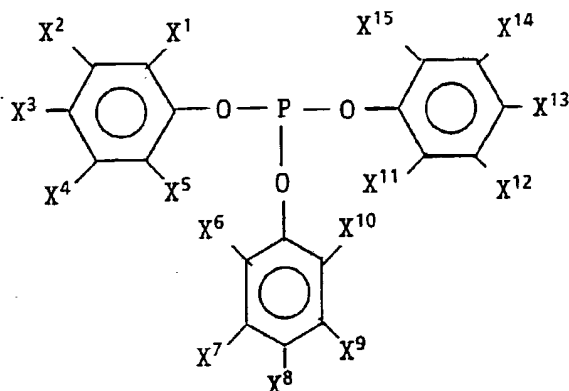
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1. A composition of matter comprising in admixture, brominated polycarbonate and about 200 parts per million to about 1,500 parts per million, by weight of the total composition, of a phosphite represented by the structure

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where X¹ to X¹⁵ is each independently hydrogen or an alkyl, aryl, alkaryl or aralkyl radical of one to ten carbon atoms.

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2. The composition of Claim 1 wherein the brominated polycarbonate is a brominated segmented block co-polycarbonate.

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3. The composition of Claim 1 wherein said phosphite is tris (2,4-di-t-butylphenyl) phosphite.

4. The composition of Claim 1 shaped in the form of a transparent apparatus.

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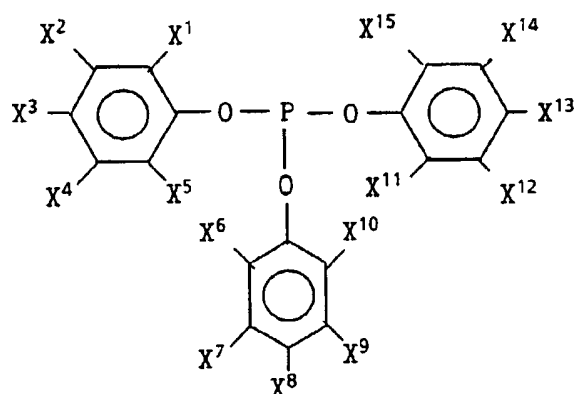
5. The composition of Claim 1 in the form of a molded article.

6. A film, sheet, article, fiber or other formed or molded object which has been thermally aged, comprising, in admixture, (a) brominated polycarbonate and (b) about 200 parts per million to about 1,500 parts per million, by weight of the total composition, of a mixture of (i) a phosphite represented by the structure

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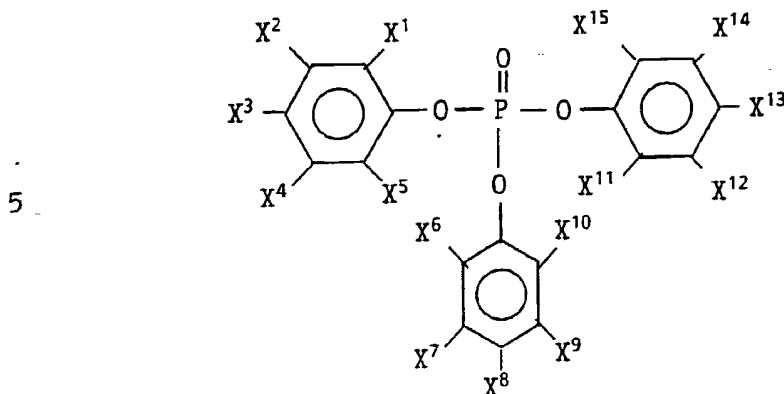
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where X^1 to X^{15} is each independently hydrogen or an alkyl, aryl, alkaryl or aralkyl radical of one to ten carbon atoms, and (ii) a phosphate represented by the structure

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where X^1 to X^{15} are as set forth above.

7. The film, sheet, article, fiber or other
15 formed or molded object of Claim 6 wherein the
brominated polycarbonate is a brominated segmented block
co-polycarbonate.

8. The film, sheet, article, fiber or other
20 formed or molded object of Claim 6 wherein said
phosphite is tris (2,4-di-t-butylphenyl) phosphite, and
said phosphate is tris (2,4-di-t-butylphenyl) phosphate.

9. The film, sheet, article, fiber or other
25 formed or molded object of Claim 6 which has a
Yellowness Index of less than 15, as measured according
to ASTM Designation D 1925-70.

30 10. The film, sheet, article, fiber or other
formed or molded object of Claim 6 which has a weight
average molecular weight, as determined by gel
permeation chromatography, of greater than 25,000.

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11. The film, sheet, article, fiber or other
formed or molded object of Claim 6 which is transparent.

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Effect of Trisaryl Phosphite Levels [in parts per million ("PPM")] on Yellowness Index during Heat Aging of Unhalogenated Polycarbonate

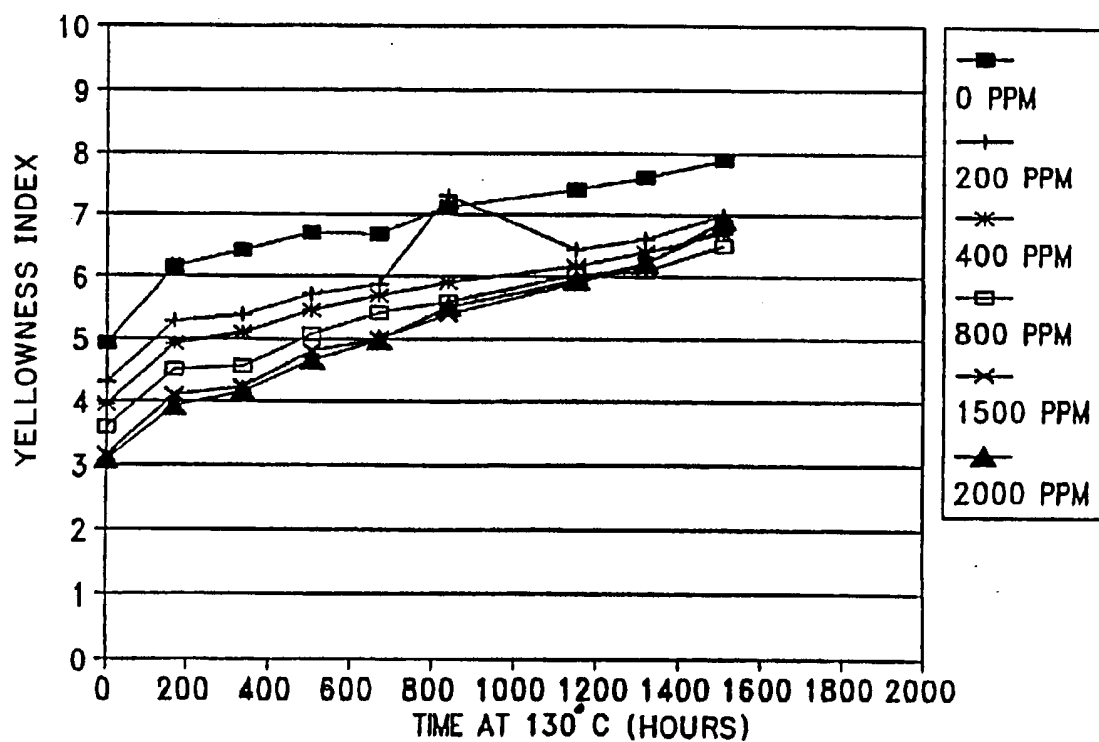


FIG. 1

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Effect of Trisaryl Phosphite Levels [in parts per million ("PPM")] on Yellowness Index during Heat Aging of Halogenated Poly carbonate

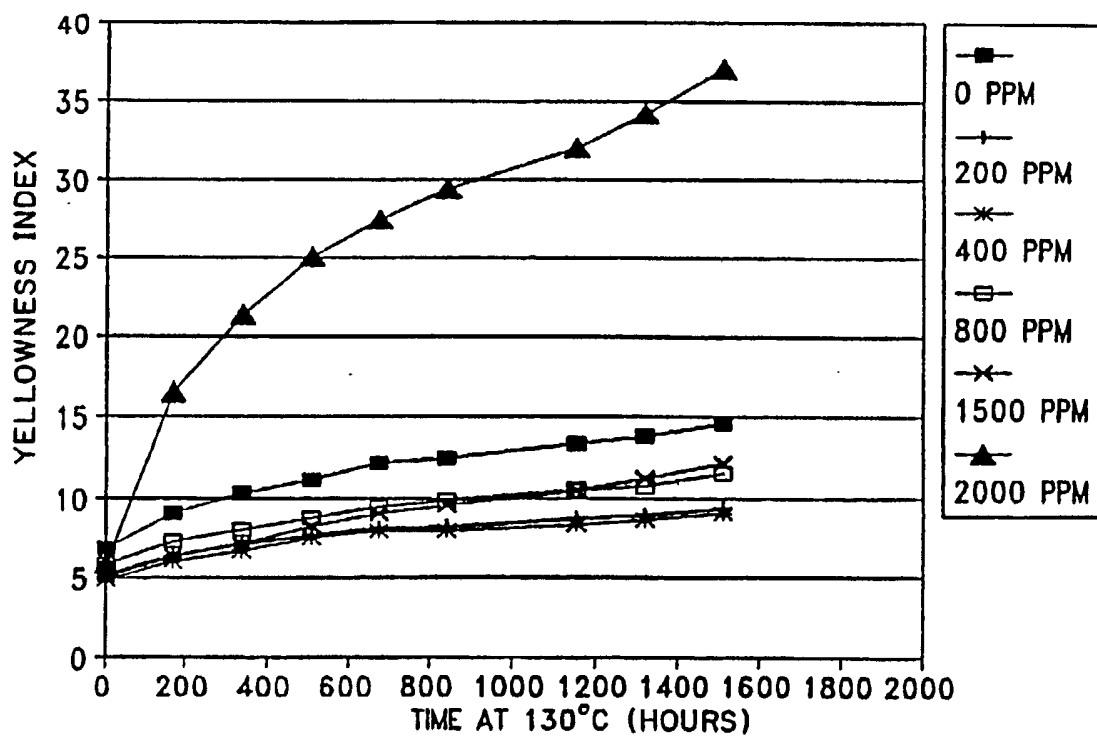


FIG. 2

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Effect of Trisaryl Phosphite Levels [in parts per million ("PPM")] on Yellowness Index at 1,512 Hours from Heat Aging of Halogenated and Unhalogenated Polycarbonate

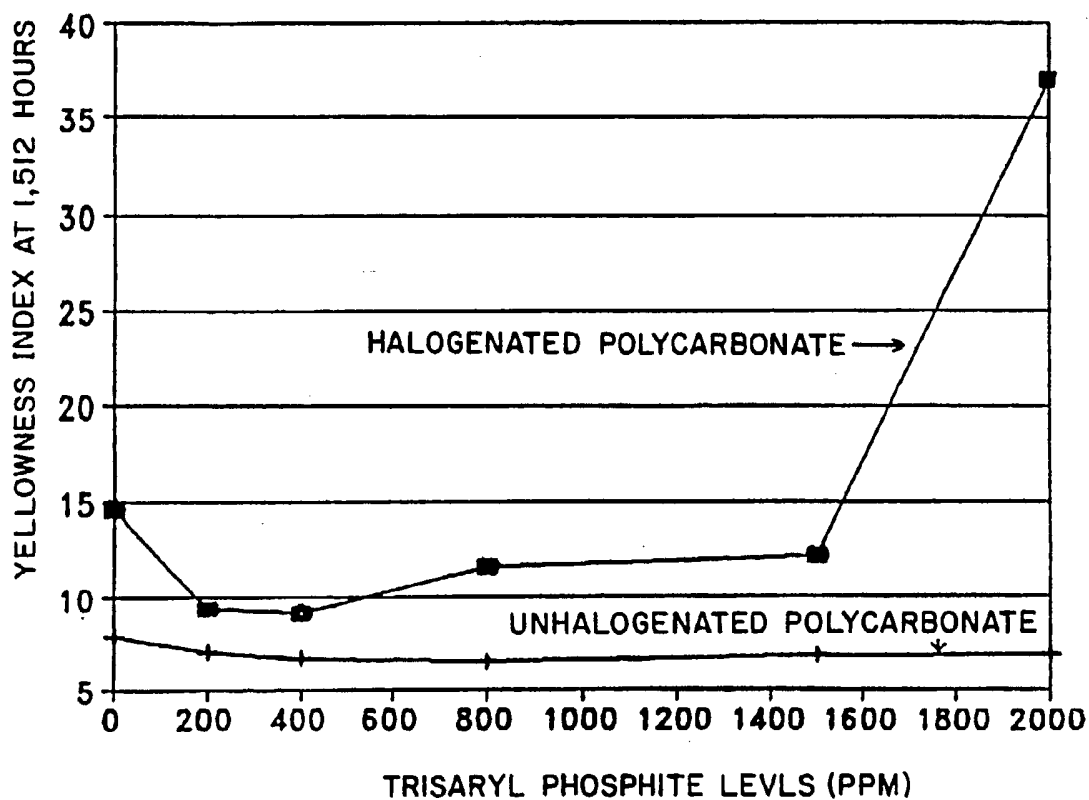


FIG. 3

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Effect of Trisaryl Phosphite Levels [in parts per million ("PPM")] on Weight Average Molecular Weight during Heat Aging of Unhalogenated Polycarbonate

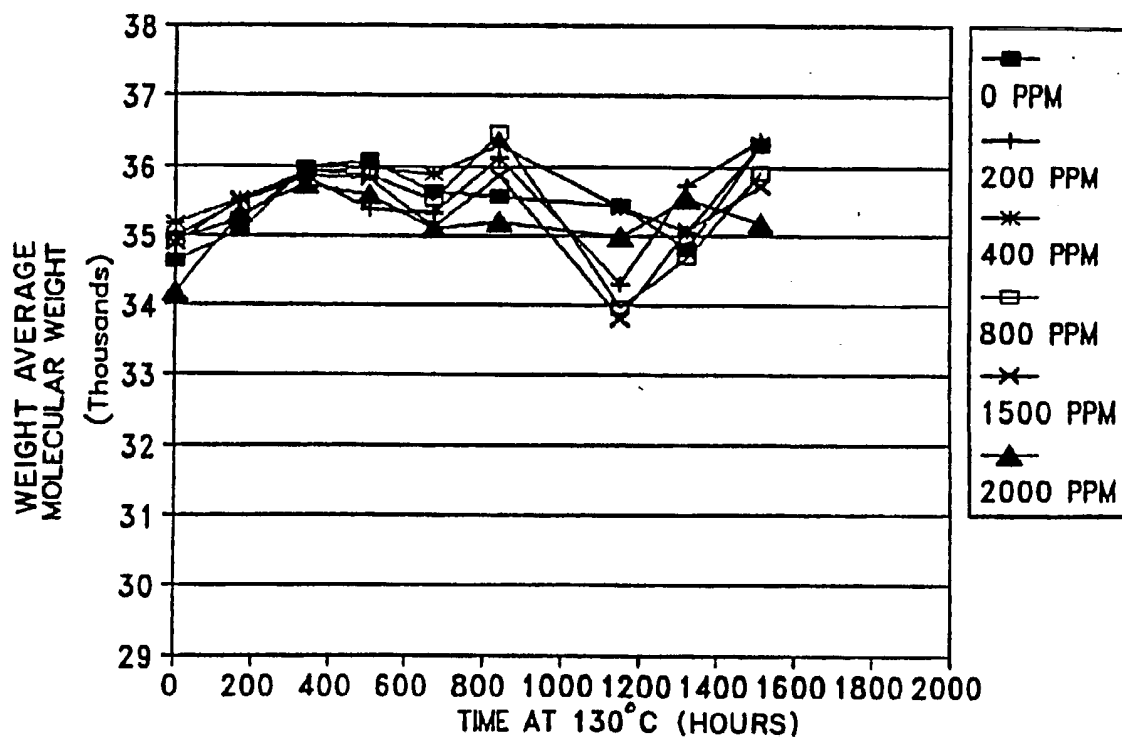


FIG. 4

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06/22/2004, EAST Version: 1.4.1

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Effect of Trisaryl Phosphite Levels [in parts per million ("PPM")] on Weight Average Molecular Weight during Heat Aging of Halogenated Polycarbonate

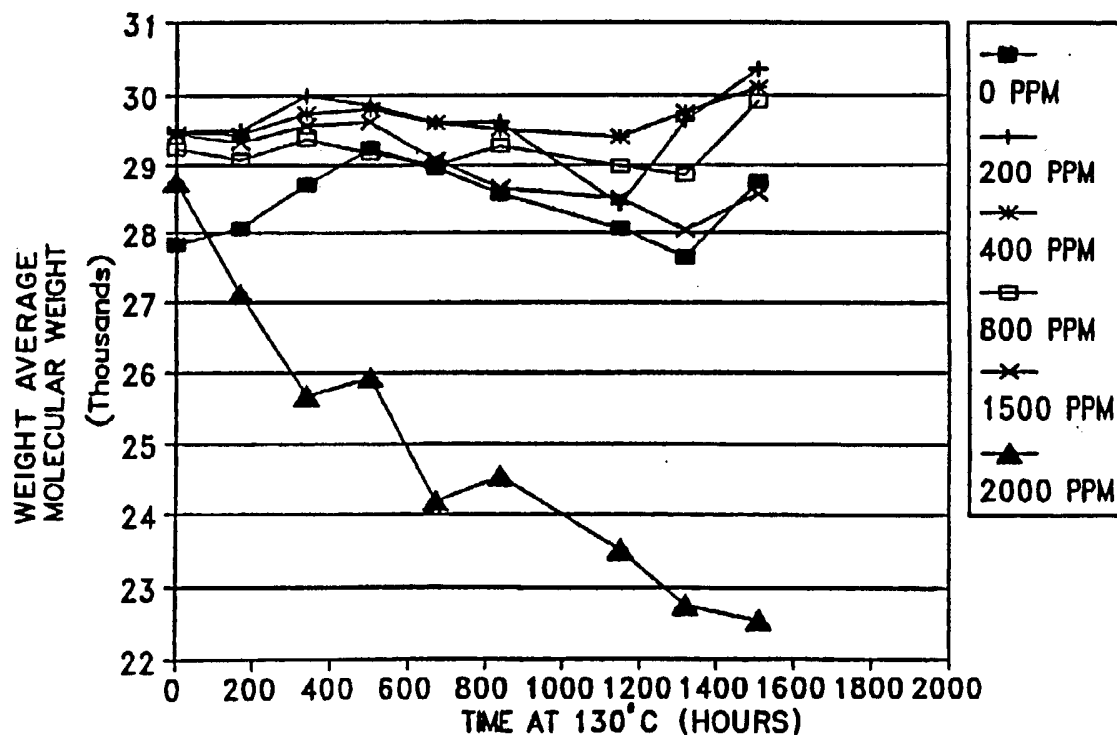


FIG. 5

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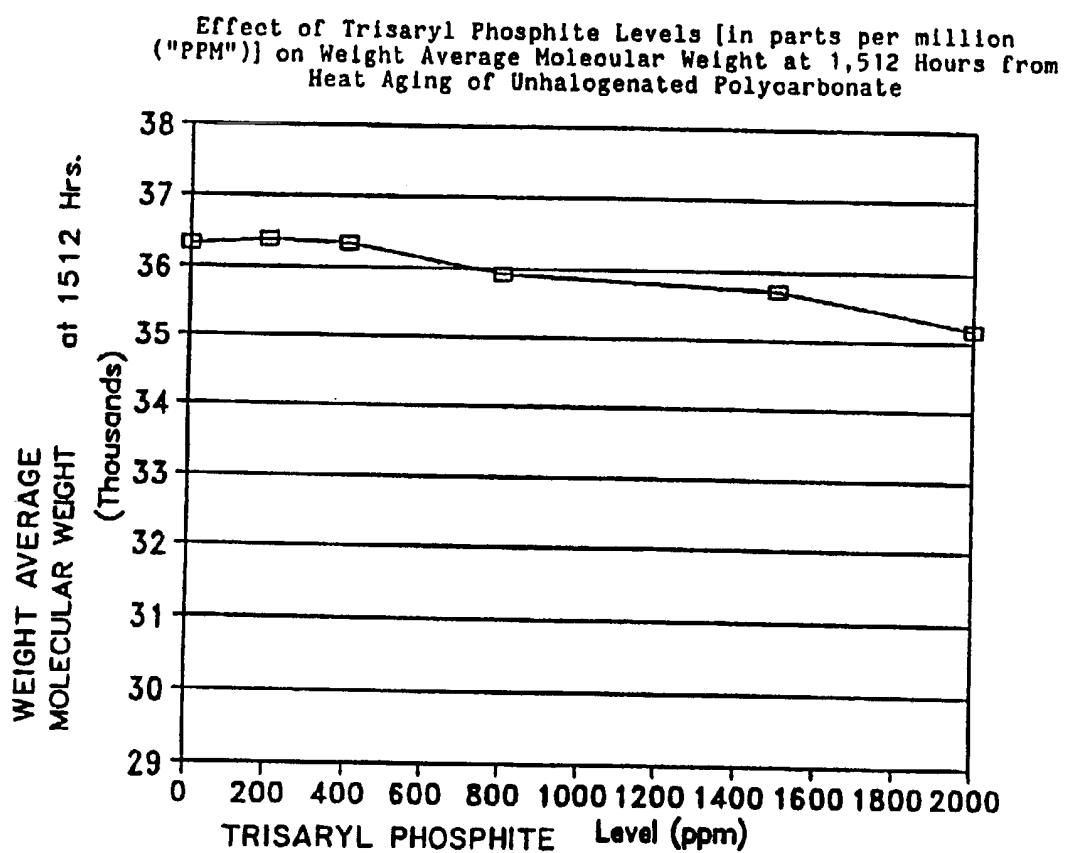


FIG. 6

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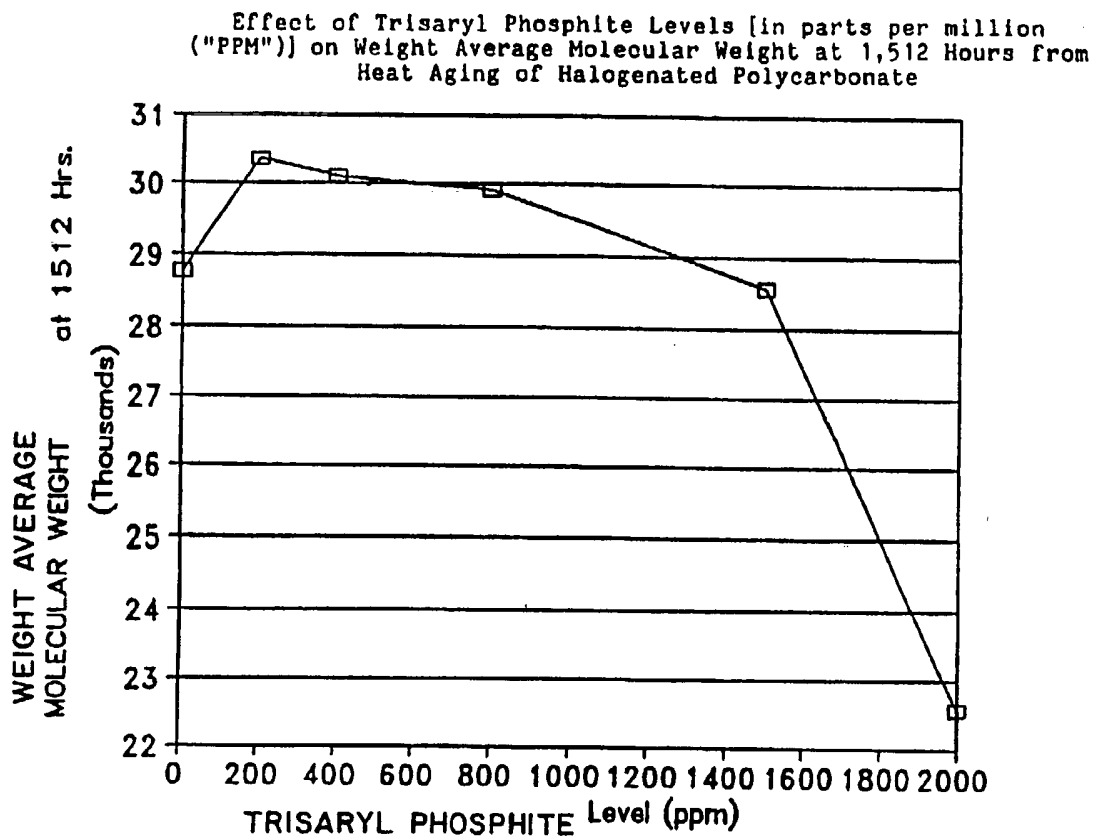


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/09623

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08L69/00; C08K5/526; C08K5/52; //(C08K5/52, 5:526,5:523)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claims No. ¹³
X	DE,A,3 346 122 (GENERAL ELECTRIC CO.) 28 June 1984 see page 3, line 10 - line 16 see page 4, line 22 - page 5, line 23 see page 6, line 18 - line 32 see page 10, line 13 - line 32 see claims 1-5 ---	1-3
A	EP,A,0 201 795 (BAYER AG) 20 November 1986 see page 8, line 21 - line 25 see examples see claim 1 ---	1,5,6
A	EP,A,0 111 791 (GENERAL ELECTRIC CO.) 27 June 1984 see claims 1,4-9 --- -/-	1,5,6
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
12 MAY 1992	19 MAY 1992	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	ENGEL S.L.H. <i>H. Engel</i>	

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	
P,A	EP,A,0 422 438 (BAYER AG) 17 April 1991 see page 1 - page 2 see page 12, line 22 - line 58 see page 16, line 8 - line 27 see claims ---	1,2,5,6

Form PCT/ISA/210 (extra sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9109623
SA 55814**

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EP-A-0201795	20-11-86	DE-A- 3516807 JP-A- 61261352 US-A- 4751260	13-11-86 19-11-86 14-06-88
EP-A-0111791	27-06-84	JP-A- 59117554	06-07-84
EP-A-0422438	17-04-91	DE-A- 3933545 JP-A- 3152154	11-04-91 28-06-91

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